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Distinct sulfur saturation histories within the Palaeogene Magilligan Sill, Northern Ireland: Implications for Ni-Cu-PGE mineralisation in the North Atlantic Igneous Province

Jordan J. Lindsay^{*1}, Hannah S. R. Hughes^{1, 2}, Dermot Smyth³, Iain McDonald⁴, Adrian J. Boyce⁵, Jens C. Ø. Andersen¹

¹ Camborne School of Mines, College of Engineering Mathematics and Physical Sciences, University of Exeter, Penryn Campus, Penryn, Cornwall, TR10 9EZ, UK.

(*jl731@exeter.ac.uk)

² School of Geosciences, University of the Witwatersrand, Private Bag 3, Wits 2050, Johannesburg, South Africa

³ Lonmin (Northern Ireland) Ltd., 6 Plasketts Close, Kilbegs Business Park, Kilbegs Road, ANTRIM, Northern Ireland, BT41 4LY, UK

⁴ School of Earth and Ocean Sciences, Cardiff University, Park Place, Cardiff, CF10 3AT, UK

⁵ Scottish Universities Environmental Research Centre (SUERC), East Kilbride, Glasgow, Scotland, G75 0QF, UK

The ~60 m thick Magilligan Sill is part of the British Palaeogene Igneous Province in the North Atlantic. The sill comprises layers of dolerite and olivine gabbro, and it intrudes a thick sequence of Mesozoic mudstones and marls, which are locally baked at the sill margins. Since 2014, the sill has been an exploration target for orthomagmatic Ni-Cu-PGE sulfide mineralisation analogous to the Noril'sk-Talnakh intrusion in Russia. We present new petrological, geochemical and S-isotope data to assess the prospectivity of the sill and the underlying magmatic plumbing system. Most sulfides in the dolerite portions of the sill are < 50 μm in size and comprise only pyrite with PGE abundances below detection limit. In the olivine gabbros, > 150 μm size pentlandite, chalcopyrite and pyrrhotite grains contain < 4 ppm total PGE, 1 460 ppm Co and 88 ppm Ag. Pyrite from the dolerites have $\delta^{34}\text{S}$ ranging from -10.0 to +3.4 ‰ and olivine gabbro sulfides range from -2.5 to -1.1 ‰, suggesting widespread crustal contamination. The S/Se ratios of sulfides in the dolerites and olivine gabbros range from 3 500 to 19 500 and from 1 970 to 3 710, respectively, indicating that the latter may have come from upstream in the magma plumbing system. The Magilligan Sill records multiple injections of mafic magma into an inflating sill package, each with distinct mechanisms towards S-saturation. Whilst the sulfide minerals in the sill do not constitute significant mineralisation themselves, detailed in-situ studies highlight a divergence in S-saturation histories, and suggest that a larger volume of olivine gabbro sulfides at depth may be prospective.

Keywords: PGE, sulfur isotopes, magma conduit system, mineralisation, North Atlantic Igneous Province

1 **Introduction**

2 Mafic-ultramafic magmatic plumbing systems in the upper crust may be highly
3 prospective for orthomagmatic sulfide mineralisation, and they host some of the largest Ni–Cu
4 and platinum group element (PGE) deposits in the world such as at Noril'sk and at Pechenga
5 in Russia (Naldrett 1997). The formation of sulfide deposits in plumbing systems requires three
6 major mechanisms: 1) The emplacement of a relatively metal-rich, initially S-undersaturated
7 mantle-derived magma from depth; 2) S-saturation of magma (normally via assimilation of
8 crustal S) and subsequent separation of immiscible sulfide from the silicate melt, followed by
9 the partitioning of chalcophile elements into the sulfide liquid; 3) Accumulation of droplets of
10 sulfide liquid forming mineralisation potentially at an economic scale (Leshner and Burnham
11 2001, Maier 2005, Maier and Groves 2011, Barnes et al. 2015). Chalcophile elements,
12 including Ni, Cu and PGE, partition strongly into sulfide phases upon the formation of an
13 immiscible sulfide liquid in a S-saturated silicate magma (e.g. Campbell and Naldrett 1979,
14 Crocket 2002, Naldrett 2004, 2010, Barnes and Lightfoot 2005). The mass ratio of silicate melt
15 interacting with sulfide liquid is described by an 'R-factor' and the mass of magma exchanging
16 siderophile metals with sulfide liquid has a strong influence on final ore composition (Campbell
17 and Naldrett 1979, Lightfoot 2007). A cumulative R-factor may be envisaged whereby
18 replenishment of a conduit system by multiple magma batches progressively upgrades the
19 sulfide tenor by allowing sulfide liquid to interact with and receive metal from large volumes
20 of silicate melt (Kerr and Leitch 2005). This process is shown to be instrumental in creating
21 conduit-hosted orthomagmatic Ni-Cu-PGE deposits such as within the Noril'sk Talnakh
22 intrusion in Russia (Barnes et al. 2016), the Platreef of the Bushveld Complex (e.g. Holwell
23 and McDonald 2007, Holwell et al. 2011, Ihlenfeld and Keays 2011), the Insizwa Complex of
24 South Africa (Lightfoot et al. 1984), and Voisey's Bay in Canada (Huminicki et al. 2008).

A silicate melt can dissolve sulfur until it reaches the threshold of sulfur content at sulfide saturation (SCSS; Shima and Naldrett 1975). Adding excess crustal sulfur via assimilation may cause a magma to exceed the SCSS, and melting of country rock sulfides can directly introduce a sulfide xenomelt into the magma (Leshner 2017). Changing the pressure, temperature, and/or oxidation state of the magma can also shift the SCSS. In either case this forces the magma to exsolve an immiscible sulfide liquid (Mavrogenes and O'Neill 1999). The S-isotopic composition of sulfide minerals (e.g., $\delta^{34}\text{S}$) in high degree mantle melts is near chondritic, while sulfides in crustal rocks are more isotopically variable (Faure 1977). Mantle $\delta^{34}\text{S}$ is typically $0.1 \pm 0.5 \text{ ‰}$ (Sakai et al. 1984), and values different from this indicate assimilation of crustal rock in a magma. A second tool for analysing the causes for sulfide saturation is the S/Se ratio of sulfides. Contrasts in S/Se are often much larger and more sensitive than $\delta^{34}\text{S}$. In the absence of crustal contamination, sulfides in mantle-derived magmas will have $\text{S/Se} < 4,000$ (Lorand et al. 2003, Lorand and Alard 2010) with typical 'mantle-like' S/Se ratios ranging from 2 850 to 4 350 (Eckstrand and Hulbert 1987). Divergence from the average mantle ranges of $\delta^{34}\text{S}$ and S/Se indicates contamination of the magma by crustal sulfur or partial oxidation of the sulfide minerals after crystallisation. Sulfur-saturation can occur multiple times and at different depths in conduit systems (e.g. Li et al. 2009, Hayes et al. 2015), and thus studies using geochemical proxies and indicators for the causes of S-saturation must take this into account. Hence, a combination of $\delta^{34}\text{S}$ and S/Se can be used to produce a more complete picture of the triggers for S-saturation (including R-factor; Leshner and Burnham 2001) and as an exploration vectoring tool towards mineralisation in orthomagmatic systems (Queffurus and Barnes 2015, Smith et al. 2016).

Platinum-group minerals (PGM) and small-scale sulfide mineralisation is documented on the Isles of Skye, Mull and Rum (Butcher et al., 1999; Pirrie et al., 2000; Power et al., 2000, as reviewed by Hughes, 2015) in the Scottish portion of the British Palaeogene Igneous

Province (BPIP). The region is part of the North Atlantic Igneous Province (NAIP), an area that has been highlighted as potentially prospective for orthomagmatic PGE mineralisation (Andersen et al., 2002). Recent studies on the islands of Skye and Rum have also highlighted extensive contamination of shallow Palaeogene intrusions by crustal S from Mesozoic sediments (Power et al. 2003, Hughes et al. 2015a, 2016), exemplified by light S-isotopic compositions of steeply dipping conduits (e.g. Hughes et al. 2015). By comparison, little research has been carried out on orthomagmatic mineralisation and S sources in the Irish portion of the BPIP.

The Magilligan Sill is a mafic intrusion on the north coast of County Londonderry, Northern Ireland. It crops out close to the western edge of the Antrim Plateau, and is part of the BPIP. While the Magilligan Sill has never been dated, ^{40}Ar – ^{39}Ar geochronology for the nearby Portrush Sill estimates an age of 54.9 ± 0.6 Ma (McKenna 2009). We speculate that the two sills are of comparable ages given their lithological similarity and their emplacement beneath the Antrim lavas and into Mesozoic sediments. Given its setting within a large igneous province, injected through a thick sequence of S-rich crustal sediments, the Magilligan Sill became an exploration target for Lonmin (Northern Ireland) Ltd, who investigated the site from 2014 to 2017. This paper presents the first detailed account of the petrology and geochemistry of the Magilligan Sill. We use sulfide-specific and bulk rock S-isotope compositions together with *in situ* sulfide major and trace element analyses of Lonmin borehole core samples from the sill to establish the causes of S-saturation in magma batches prior to emplacement into the intrusion. We use this to assess the prospectivity of the sill itself as well as that of the surrounding magmatic plumbing system, using Noril'sk as an analogue.

Regional Geology

The North Atlantic Igneous Province formed during a period of continental flood basalt magmatism as the proto-Icelandic mantle plume impinged upon the thick continental lithosphere under the North Atlantic and Rae Cratons, and adjoining orogenic belts. Continental flood basalt magmatism (both tholeiitic and alkalic) initiated c. 62 Ma across what is now Greenland and Baffin Island, and the UK and Ireland (in the form of the BPIP), and associated rifting ultimately led to the opening of the Atlantic Ocean (Saunders et al. 1997). BPIP lavas were erupted over a timespan of approximately 3 Myr (61-58 Ma; White and Lovell 1997). Several volcanic disconformities within the now eroded lava fields (Single and Jerram 2004) juxtapose lava batches that were fed by multiple volcanic centres or fissure systems (Jerram and Widdowson 2005).

Palaeogene lavas

In Northern Ireland, the geology of County Antrim and the eastern edge of County Londonderry is dominated by onshore lava fields of the BPIP. Along with the Isles of Skye and Mull in Scotland, Antrim hosts some of the best-preserved examples of Palaeogene flood basalts in the North Atlantic region (Wilson 1972, Kerr 1997). The Antrim Plateau lavas cover roughly 3 800 km² and are stratigraphically separated into the tholeiitic Lower and Upper Basalt Formations (Lyle and Patton 1989) – Figure 1. The up to 531 m thick Lower Basalts were erupted at 62.6 ± 0.6 Ma (Ganerød et al. 2011). They become more intermediate in composition up-sequence (Lyle and Patton 1989), including isolated interbasaltic rhyolite extrusions in the Tardree Mountains in the centre of the Lower Basalts (Ganerød et al. 2011). The up to 346 m thick Upper Basalts were erupted at 59.6 ± 0.6 Ma and they mark a return to more primitive compositions (Ganerød et al. 2011).

The thickest and most extensive lava field in the Scottish portion of the BPIP on the Isle of Mull is estimated to be 1800 m thick, covering approximately 840 km² (Emeleus and

Bell, 2005). In contrast to the Antrim lavas, the Mull Lavas have been divided into three principal groups (in chronological order; the transitional tholeiitic-alkalic Mull Plateau Group, the Coire Gorm type lavas, and the Central Mull Tholeiites) according to the petrogenetic and geochemical characterisation of Kerr (1993, 1995). For the Antrim lavas, it has been postulated that the reappearance of tholeiitic mafic magma was the product of a later, more extensive melting event within the proto-Icelandic plume source (Lyle 1985, 1988). However, a more recent interpretation of the changing magmatic regime of the plume, as represented by the Mull lavas, was proposed by Kerr (1993, 1995) and Kerr et al. (1999) who identified a change from small degrees of partial melting of a deeper, garnet-bearing mantle source to progressively higher degrees of partial melting of a shallower and depleted spinel-bearing mantle.

Palaeogene magma plumbing systems

Palaeogene igneous intrusions are emplaced into most levels of the Mesozoic stratigraphy in Northern Ireland. NW-SE trending dyke swarms detected by magnetic surveys occur under much of the Antrim Plateau (GSNI 2004), and are analogous to those observed in the Scottish portions of the BPIP. Dolerite sills intrude Mesozoic sedimentary rocks exposed along the north Antrim coast, including the Portrush and Magilligan Sills (Wilson 1972) (Fig. 1). The Portrush Sill is the more studied of these two intrusions, with work published on its petrology and country rock contact metamorphism (Ledevin et al. 2012). The Portrush Sill comprises a highly altered olivine gabbro with thin aphanitic chilled margins. As the sill intruded, it baked the surrounding Jurassic siltstones to cordierite hornfels facies for ~10 m from the intrusion margins (Ledevin *et al.*, 2012). It is younger than the Antrim Plateau Lavas (54.9 ± 0.6 Ma; McKenna, 2009), consists of a main sill with two smaller sills above it, and is estimated to be 45-60 m thick. Unlike intrusions at Noril'sk or Pechenga, the Portrush Sill is thought not to have fed a large volume of magma to the surface.

The Magilligan Sill (Fig. 1, 2), first documented in the subsurface via drilling during a Mineral Reconnaissance Programme drilling campaign (BGS 1964), has rarely been mentioned in the literature. Wilson (1983) describes it as a ~60 m thick dolerite sill emplaced into Jurassic Lias mudstones, which are underlain by Triassic and Permian sediments (Fig. 2). There is no published geochronological or geochemical data available for the sill.

By contrast, there is an abundance of published literature on the petrology and magmatic development of the Trotternish Sills and Shiant Sill (Fig. 1) of the Isle of Skye and Shiant Isles, respectively (Scottish BPIP). Like the Magilligan and Portrush Sills, the Trotternish Sills and Shiant Sill are not contemporaneous with the adjoining lava field (Skye lava field). The Trotternish Sills are 250 m thick, comprising individual sub-alkaline intrusions, up to 130 m thick (Gibson 1990). The sills contain ‘fingers’ or horizons of picrites, picrodolerites and crinanites, many of which have chilled margins (Gibson and Jones 1991). The Shiant Sill lies further west and is more alkaline than the Trotternish Sills, but is similar in thickness and also contains multiple intrusive units (Gibson and Jones 1991). The Shiant Sill is dominated by crinanites and picrodolerites with infrequent metre-thick picrite horizons (Gibb and Henderson 1984). The sills in both localities are thought to have formed from discrete pulses of differentiating alkali-basalt magma being injected into the sill from a single, chemically zoned chamber beneath the sill complex (Gibson and Jones 1991). The geology of the Magilligan, Portrush and Trotternish Sills is compared in Figure 3.

Mesozoic sedimentary basin

The Palaeogene intrusions were emplaced into sedimentary rocks of the British Hebridean basin and as such, the country rocks are similar in both Northern Ireland and Scotland. The Magilligan and Portrush Sills in Northern Ireland intrude the Lower Jurassic Waterloo Mudstone Formation of the Lower Lias Group (GSNI 2004), whereas the Trotternish

Sill intrudes the Middle Jurassic Lealt Shale and Valtos Sandstone Formations of the Great Estuarine Group (Woodcock and Strachan 2012) (Fig. 3). The Shiant Sill intrudes Lower Lias Group sediments, a large raft of which separates the intrusion into two bodies that were previously thought to be distinct (Gibb and Henderson 1984). Intermittent evaporite horizons are common within the Mesozoic northern British basin (GSNI 2004). The entire Mesozoic succession in Britain represents a S-rich source that could have contaminated and assimilated Palaeogene intrusions.

Geology of the Magilligan Sill

The Magilligan Sill has a chilled upper margin of aphyric to very fine-grained, normally olivine-deficient dolerite, present in all exploration boreholes, below which is a 5 m thick zone of vesicular fine-grained dolerite (Fig. 4). The sill coarsens gradually to become a gabbro 10-20 m from the intrusion margin, with rare olivine identified in the majority of the drill core. Green-tinged (more olivine-rich), 1-5 m thick layers, that are distinct from the dark grey gabbros, occur sporadically throughout the sill. Within the bottom 10 m of the sill, the grain size decreases progressively to form a lower chilled dolerite margin with abundant vesicles in the lowermost 1-2 m. Rafts of baked sediment occur within the intrusion, and < 1 m isolated zones of dolerite occur within the country rock outside the main intrusion. Multiple layers of dolerite/gabbro form individual units in the intrusive sequence (Fig. 4). Each unit coarsens downwards and displays a range of crystal sizes across their thickness, but overall the centre of the sill is significantly coarser than the margins. The country rock surrounding the sill comprises mudstone with occasional phosphatic and sandy units, and is notably baked and metamorphosed to hornfels in the 1-3 m immediately next to the sill contact. Outwith the baked contacts, the mudstones are dark grey, fissile and pyrite-rich. Proximal to the sill, baked mudstones are very fine grained, cordierite facies slates with visible fine pyrite.

Methodology

A total of forty-seven half or quarter diamond drill core samples were collected for this study from three Lonmin boreholes that intersect the sill and the overlying and underlying Mesozoic sedimentary rocks. These boreholes are referred to here as “Boreholes 1, 2 and 3”, and their locations are shown in Figure 2. Table A1 (see Supplementary Material) gives a full list of hand specimen descriptions for all drill core samples.

Microscopy and mineral analysis

Transmitted and reflected light optical microscopy was undertaken at Camborne School of Mines (CSM), University of Exeter, using a Nikon Eclipse E600 Pol microscope with Nikon Digital Sight 5MP camera on 12 polished thin sections prepared from the Magilligan Sill drill core samples and its country rocks.

Quantitative mineral analysis was undertaken on eight of the polished thin sections of the sill samples at CSM with a JEOL JXA-8200 Electron Microprobe (EPMA), using a Wavelength Dispersive Spectrometer (WDS). Silicate and sulfide standards were used to calibrate for major elements Si, Na, Cr, K, Al, Mg, Mn, Ca, Fe, Ni, Zn, Ti and V, and Fe, S, Ni, Pb, Co and Cu, respectively. Standard analyses and results are shown in Table S1 (silicates and sulfides) (see Supplementary Material). The beam parameters were 15 nÅ, at 15 kV for thin section samples 1, 5, 6 and 7, and 1 nA at 20 kV for thin section samples 2, 3, 8, and 10. Major elements (Si, Na, K, Al, Mg, Mn, Ca, Fe, S) had counting times of 20 s peak and 10 s background, while minor/trace elements (Cr, Ni, Zn, Ti, V, Pb, Co, Cu) were 30 s peak and 15 s background. Backscattered electron images were taken separately using the same instrument.

LA-ICP-MS

Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) was undertaken at the School of Earth and Ocean Sciences, Cardiff University, on polished thin

sections using a New Wave Research UP213 UV laser system with a Thermo X Series 2 ICP-MS. Laser analyses were utilised in order to investigate the trace element content of individual sulfide grains *in situ* within samples, with the beam moving across mineral surfaces linearly. The beam size was 40 μm , using a 10 Hz current with a power of $\sim 6 \text{ J cm}^{-2}$ and an average ablation rate of $6 \mu\text{ms}^{-1}$ along a programmed linear route. Acquisition times ranged from 70 to 150 s, with longer times for larger sulfides (according to laser line length), with an additional 40 s per acquisition to accommodate gas blank measurement and chamber flushing/evacuation. Calibration was conducted using three in-house sulfide standards of known compositions developed at Cardiff University (for further details see Prichard et al. 2013, Smith et al. 2014). Major elements ^{57}Fe , ^{61}Ni and ^{65}Cu , and trace elements ^{59}Co , ^{66}Zn , ^{75}As , ^{77}Se , ^{95}Mo , $^{99, 101}\text{Ru}$, ^{103}Rh , $^{105, 106, 108}\text{Pd}$, ^{109}Ag , ^{111}Cd , ^{121}Sb , ^{125}Te , ^{185}Re , ^{189}Os , ^{193}Ir , ^{195}Pt , ^{197}Au , ^{206}Pb and ^{209}Bi were calibrated using these standards. Sulfur concentrations were assumed based on sulfide mineralogy. Following calibration, the Memorial Pyrrhotite Po724 standard was run as an unknown to check machine accuracy. An internal pyrite standard was analysed as a qualitative comparison for stoichiometric S values of pyrite, pyrrhotite, pentlandite and chalcopyrite. The results of each stage of calibration are shown in Table S2 (see Supplementary Material).

Sulfur isotopes

Sulfur isotope analyses were undertaken at the Scottish Universities Environmental Research Centre (SUERC), University of Glasgow. A representative subset of six sill samples and five sediment samples were selected for conventional sulfur isotope analysis. Individual sulfide crystals were handpicked from within sedimentary samples for analysis. Sill samples were crushed using a standard jaw crusher, sieved and manually ground into a powder, with as little silicate material as possible. 5 mg of each powdered sample was added to 200 mg of CuO powder (for a single analysis) and the compound was homogenised using a mortar and pestle, and stored in a glass pellet. For sill samples, due to the small sulfide size, a Frantz Magnetic

Barrier Lab Separator was used to separate most of the silicate minerals, retaining the sulfides (mainly the paramagnetic pyrrhotite) for blending with the CuO powder. The compound samples were then combusted in their glass pellets at 1020 °C, and the gas emitted was extracted into a vacuum line. Water was frozen off in acetone and dry ice, and SO₂ and CO₂ were separated by a multistage freeze-thaw system using liquid nitrogen and N-pentane. SO₂ was collected at the end of the process, and detected by a ThermoFisher Scientific MAT 253 dual inlet mass spectrometer. The spectrometer measures the abundance of ³⁴S and ³²S in the gas, giving a relative ratio of the two isotopes ($\delta^{34}\text{S}$). The ratio was compared to an in-house SO₂ gas standard of known $\delta^{34}\text{S}$. The raw $\delta^{34}\text{S}$ was then calibrated using the Vienna Canyon Diablo Troilite (VCDT) global $\delta^{34}\text{S}$ standard for sulfur isotope analysis, and results reported in ‰ relative to the VCDT. Multiple runs of two powdered international standards (chalcopyrite CP-1, -4.56 ‰; sphalerite NBS-123, +17.1 ‰) and one in-house standard (silver sulfide IAEA-S-3, -32.2 ‰) were analysed using the conventional sulfur gas extraction line as unknowns prior to sample analysis to test calibration accuracy. Standard analyses were repeated twice to establish data precision. Standard calibration results and sample repeats are shown in Table S3 (see Supplementary Material).

Results

Petrology

The locations of thin section samples T1-12 with respect to Boreholes 1-3 are shown in Figure 4. Dolerites at the topmost sill contact (e.g., T1, 4, 5 and 6) generally have a very fine-grained almost aphanitic groundmass (<100 µm), and are primarily composed of subophitic semi-chloritized augite and anorthite (highly altered to zeolites and clays), with infrequent olivine phenocrysts (completely or partially serpentinised or chloritized). Dolerites below this ~2 m chilled margin contain 200 to 700 µm diameter zeolite-quartz-calcite-filled vesicles over

242 a depth interval of approximately 5 m. The lowermost contact of the sill (T10 and 12) is
 243 texturally and mineralogically similar to the top one, with a 1 m thick chilled margin and a 3
 244 m thick vesicular zone. Augite, anorthite and altered olivine phenocrysts dominate the very
 245 fine-grained groundmass. Chlorite is abundant, not only partially replacing mafic minerals but
 246 also appearing interstitially, in fractures, and as part of the matrix. In the top and lower sill
 247 contacts, small spinels ($<500\text{ }\mu\text{m}$ and ranging titanomagnetite to ilmenite) make up $>5\%$ of the
 248 rock.

249 Inwards from the contact zones, the sills become coarser (mm-scale crystals) and thus
 250 are classed as gabbros. However, individual segments of the sill package vary considerably in
 251 their mineralogy – for example, T2 and 3 of Borehole 3 are simply coarser versions of the rocks
 252 found at the top contact of the sill (gabbros), whereas T7 and 8 of Borehole 1 are distinct with
 253 a notably higher olivine content (olivine gabbros). The olivine gabbros in the core (observed
 254 in mainly in Borehole 1, with sub-metre thick sections in Borehole 3) have their own chilled
 255 margins (10-20 cm thick) and glassier olivine crystals at the edge. In general, clinopyroxene
 256 and plagioclase are the major components of all gabbros (40-50 % and 25-40 % respectively).
 257 Olivine gabbros contain $>30\%$ olivine, which is reasonably fresh and with minor iddingsite
 258 within fractures (Fig. 5a). Olivine found in gabbros (5-10 % of their composition) is always
 259 serpentinised (Fig. 5b). Orthopyroxene occurs in T2 only with an abundance of $<5\%$. As seen
 260 in the chilled margins, spinels in the central portions of the sill are an intricate mix of
 261 titanomagnetite and ilmenite (and equigranular with surrounding groundmass silicates, on a
 262 millimetre-scale).

263 Sulfide minerals are observed with variable abundances throughout all units and
 264 lithologies in the sill. The upper and lower contact zones and the coarser gabbro sections of the
 265 sill host trace ($<1\%$) interstitial small grains (averaging $\sim 50\text{ }\mu\text{m}$) of pyrite and pyrrhotite only
 266 (Fig. 5c). Chalcopyrite and bornite ($<70\text{ }\mu\text{m}$) are found in very rare instances. By contrast, the

olivine gabbro units contain a mixture of sulfides (generally $>150\ \mu\text{m}$) in higher proportions (1-2 %) including pyrite, pyrrhotite, chalcopyrite, pentlandite, and galena – normally in complex intergrowths (Fig. 5d). Sulfides in the olivine gabbros are often partially oxidised (10-20 % around rims) with skeletal grain shapes due to dissolution. In comparison, sulfides in the gabbros are generally fresher ($< 5\%$ surface alteration). No platinum group minerals (PGM) are observed in the samples.

Mineral chemistry

Silicates

The major element compositions of clinopyroxenes in the sill are distinct between gabbros and olivine gabbros (Fig. 6a-b) – the olivine gabbros contain magnesian and/or calcic pyroxenes (14.0-15.5 wt. % MgO, 22.0-22.5 wt. % CaO and 5-7 wt. % FeO), whereas all other pyroxenes are more iron-rich (7-11 wt. % FeO, with 12-14 wt. % MgO and 20.5-22.0 wt. % CaO). As such, olivine gabbro clinopyroxenes are less augitic, with Mg, Ca, Fe, and Al bearing varieties found in T7 and 8. Individual pyroxenes in the olivine gabbros are often compositionally zoned. Olivine in olivine gabbros have Fo% of ~ 65 compared to ~ 50 in (unserpentinised) olivine in other sill lithologies. Plagioclase is systematically more anorthitic in olivine gabbros with mean An% of 82, compared to 70 in the gabbros. A full list of major element concentrations can be found in Supplementary Table S4.

Sulfides

A summary of major and trace element compositions of sulfides from the Magilligan Sill and surrounding country rocks obtained from LA-ICP-MS are presented in Table 1, with the full list displayed in Supplementary Material Table S2. Figures 7a-d summarise the trace element geochemistry of sulfides found in the Magilligan Sill. Cobalt is concentrated in olivine gabbro sulfides, with the highest amounts ($< 2\ 700\ \text{ppm}$) found in pentlandite; the average Co

291 concentration across all olivine gabbro sulfides above detection is 1 460 ppm. Silver is present
 292 between 2.3 and 315 ppm in olivine gabbro sulfides (highest in pentlandite, although also
 293 present in chalcopyrite), with an average of 88 ppm across all olivine gabbro sulfides above
 294 detection. Sulfides excluding those in the olivine gabbros contain < 0.12 ppm Re, < 570 ppm
 295 Co and < 5.3 ppm Ag. Figures 7a and 7b show a slight positive correlation between Ni
 296 concentrations and Co/Ag concentrations in sulfides. The PGE are below detection in pyrite
 297 from dolerites (from the upper and lower contact zones) and gabbros throughout the sill
 298 package. By contrast, sulfides in the olivine gabbros contain up to 4 ppm total palladium-group
 299 PGE (PPGE; Rh, Pt and Pd), and up to 0.24 ppm iridium-group PGE (IPGE; Os, Ir and Ru). In
 300 T7 and 8, Ru and Rh are only found in chalcopyrite grains (average of 0.2 and 0.65 ppm,
 301 respectively). The remaining PGE are found in both chalcopyrite and pentlandite (Fig. 7c-d):
 302 Pd is more abundant in chalcopyrite (0.25 – 2.43 ppm); Pt is more abundant in pentlandite (0.03
 303 – 0.66 ppm); and Os and Ir have been recorded close to background in both minerals between
 304 0.02 and 0.05 ppm. Rhenium is also more abundant in olivine gabbro chalcopyrite and
 305 pentlandite than pyrite from other gabbros and dolerites (0.04 – 0.96 ppm compared to a
 306 maximum of 0.12 ppm, respectively). The absence of visible PGM suggests that PGE are found
 307 within sulfide structures.

308 Selenium concentrations for Magilligan sulfides are plotted against Ni and total PGE
 309 concentrations (from Table S2, Supplementary Material) in Figures 8a-c. Olivine gabbro
 310 sulfides have Se concentrations between 91 and 171 ppm, with S/Se ratios between 1 980 and
 311 3 720. Sulfides in the remainder of the sill have Se concentrations between 21 and 95 ppm (if
 312 above the detection limit), and S/Se ratios ranging from 3 510 to 25 200. Sulfides in the local
 313 sediment have Se concentrations between 49 and 99 ppm, and S/Se ratios of between 5 390
 314 and 10 800. In a comparison between S/Se and total PGE concentrations (Fig. 8c),
 315 chalcopyrites in the olivine gabbros tend to have S/Se ratios of 1 980 – 3 340 and total PGE

concentrations of 0.6 – 3.7 ppm. Pyrrhotites and pentlandites are similar in terms of S/Se (~ 2 700–3 700), but pentlandite tends to have higher total PGE (< 2.5 ppm). The absence of the highest S/Se values in Fig. 8a-c reinforces the fact that sulfides with high S/Se (e.g. gabbros, marginal dolerites and sediment) have, in almost all cases, no detectable PGE or Ni.

Sulfur isotope compositions

A summary of $\delta^{34}\text{S}$ compositions for the Magilligan Sill and surrounding country rock is shown in Table 2 (full dataset in Supplementary Table S3) and Figure 9a. Mesozoic shales adjacent to the sill have $\delta^{34}\text{S}$ values ranging from -10 to +5.3 ‰ above the intrusion and from -20.4 to -14.9 ‰ below it. Dolerites at the intrusion edge have $\delta^{34}\text{S}$ values between -9.6 and -2.5 ‰, whereas gabbros are consistently +3.4 ‰. Olivine gabbros have $\delta^{34}\text{S}$ values from -2.5 to -1.1 ‰.

Combined $\delta^{34}\text{S}$ and S/Se data (from the LA-ICP-MS dataset) are displayed in Figure 9b. S/Se and $\delta^{34}\text{S}$ values of the sill and its surroundings can be compared to the magmatic norm for each parameter. Only olivine gabbro samples overlap the ‘magmatic’ boundaries of S/Se (2 850–4 350; Eckstrand and Hulbert 1987, Queffurus and Barnes 2015) and $\delta^{34}\text{S}$ (0.1 ± 0.5 ‰; Sakai et al. 1984), highlighted by the hatched square in Figure 9b. S/Se values for the olivine gabbros and sediments are more restricted compared to the wide ranges observed in the dolerites and gabbros. In general, sulfides in the dolerites and gabbros have S/Se ratios 2–5 times that of the maximum magmatic norm (up to 20 000 compared to less than ~4 000). Figure 10 presents a downhole log of the Magilligan Sill in terms of S/Se ratios, S isotopes and trace element concentrations in sulfides. High PGE, Ni, Cu and Ag contents are confined to the olivine gabbro sulfides only, and S/Se and $\delta^{34}\text{S}$ downhole trends appear to mirror each other.

Discussion

Magmatic history of the Magilligan Sill

340 The Magilligan Sill has a coarse gabbroic interior and chilled doleritic margins, fitting
 341 well with descriptions of similar sills found within the BPIP – the Portrush Sill, of a similar
 342 thickness and mafic petrology (Ledevin et al. 2012); and the thicker Trotternish Sills, with
 343 distinct chemical changes throughout (Gibson 1990, Gibson and Jones 1991). As the magma
 344 intruded the Mesozoic Waterloo mudstones (Fig. 11a), the outermost parts of the sill would
 345 have cooled rapidly, resulting in the very fine-grained and vesicular dolerites seen in T1, 4, 5
 346 and 6 (top), and T10 and 12 (bottom). Heat transfer from the sill would have simultaneously
 347 metamorphosed country sediment to cordierite hornfels facies (Fig. 11b), in a similar fashion
 348 to the Portrush Sill (Ledevin et al. 2012). Following intrusion, water from an external source,
 349 potentially meteoric, altered olivine and plagioclase in the crystallised sill to produce hydrous
 350 silicates (Fig. 11c). The inwards gradation to coarser grained rocks (T2 and 3) is observed in
 351 all three boreholes, which contain similarly altered augite, anorthite, and titanomagnetite-
 352 dominated compositions in all but the olivine gabbro samples that occur sporadically
 353 throughout the sill. These olivine-rich portions (e.g. T7 and 8) feature large, reasonably fresh
 354 olivine crystals, and are chemically and texturally distinct from the rocks found elsewhere in
 355 the sill. Their pyroxenes are Mg- and Ca-rich as opposed to Fe-rich, their plagioclases are more
 356 anorthitic than albitic, and they are less pervasively altered. The abrupt nature of the marked
 357 downhole petrological changes from dolerite/gabbro to olivine gabbro indicates that the
 358 variation is not gradational, and the presence of fine, glassy margins within olivine gabbro
 359 sections implies that they were chilled against already solidified and cooled dolerites and
 360 gabbros. Hence, we conclude that the olivine gabbros are formed from new pulses of primitive
 361 magma emplaced into the earlier and already altered gabbro-dolerite sill to form distinct
 362 olivine-rich horizons observed in the sill (Fig. 11d).

363 In the Magilligan Sill, the clinopyroxene-plagioclase dominated rocks are more altered
 364 and superseded by fresher modal olivine melts, inconsistent with Bowen's discontinuous

reaction series, in which high temperature olivine crystallisation normally precedes clinopyroxene and plagioclase crystallisation in a cooling system (Bowen 1979). The more forsteritic olivine and anorthitic plagioclase in the olivine gabbros also suggest higher temperature crystallisation. We suggest that the magmatic system was replenished by younger, more primitive mantle melts following the initial emplacement of gabbros and dolerites, or that the olivine-rich horizons were formed from a completely different magma. It is unlikely that the entire magma source changed, given the localised nature of the sill, and thus re-introduction of mafic melts into a deeper magma reservoir is the preferred scenario.

We envisage that the Magilligan Sill developed in a similar manner to the Trotternish Sills. A stepwise decrease in MgO content throughout the petrological units of the Trotternish Sills from oldest to youngest (40 % in picrites, 20-10 % in picrodolerites, and 5 % in crinanites) reflects an evolving magma system with each unit injected in discontinuous pulses (Gibson 1990). The Skye lava field ranges in composition from basalt and picrobasalt to hawaiite and mugearite, also suggesting a differentiating source during Palaeogene volcanism (Hughes et al. 2015b). Internal chilled margins within the Trotternish Sills and Shiant Sill reinforce the idea of multiple injections – these are also present within the Magilligan Sill. If a magma chamber were replenished between units, subsequent magma compositions would be more mafic than the previous one (provided the influx is volumetrically significant relative to the resident magma). This is observed in the increasingly mafic, late-stage Mull lavas (Kerr 1997). The presence of multiple magma injections within equivalent sills across the BPIP and the presence of olivine in the centre of the Magilligan Sill suggests that they are formed by similar petrogenic processes. The Antrim Plateau Lavas and the Magilligan Sill follow similar evolutionary trends towards mafic (magnesian) compositions from Lower to Upper Basalts, and from gabbro to olivine gabbro, respectively.

S-saturation and the formation of sulfides

Magmatic sulfides typically have $\delta^{34}\text{S}$ values of $0.1 \pm 0.5 \text{ ‰}$ (Sakai et al. 1984). Some modern studies of MORB lava sulfides suggest larger ranges (Eckardt 2001, Seal 2006, Labidi et al. 2012), but the original values presented by Sakai *et al* account for seafloor sulfate/sulfide fractionation and are thus more precise and reliable (Leshner 2017). The local pristine magmatic $\delta^{34}\text{S}$ signature of the Scottish BPIP has been found to be $-2.3 \pm 1.5 \text{ ‰}$ (Hughes et al. 2015a) based on the mean composition of the picritic Trotternish Sills (Hughes et al. 2015a), which is comparable with that of Icelandic basalts (Torssander 1989) and MORB (Labidi et al. 2012). The Magilligan Sill sulfides record values between -9.6 and -1.1 ‰ , and one sample (T2) has $+3.4 \text{ ‰}$. Sulfides in local sediments adjacent to the sill record average $\delta^{34}\text{S}$ values of -6.0 ‰ (above the sill) and -17.7 ‰ (below the sill). It follows that most of the sill magmas have experienced some degree of crustal contamination, as the addition of isotopically light crustal sulfur from the Mesozoic country rocks will shift their primary magmatic sulfide signature (assumed to be -2.3 ‰ for the BPIP; Hughes *et al.*, 2015). Based on work on the Trotternish Sills (Hughes et al. 2015a), the proportion of sedimentary sulfur assimilated by the magma (f) can be calculated, using the observed $\delta^{34}\text{S}$ values achieved in the contaminated sill ($\delta^{34}\text{S}_{\text{mix}}$) using the following equation:

$$\delta^{34}\text{S}_{\text{mix}} = \frac{\delta^{34}\text{S}_c X_{cf} + \delta^{34}\text{S}_m X_m (1 - f)}{X_{cf} + X_m (1 - f)}$$

Here, $\delta^{34}\text{S}_m$ and $\delta^{34}\text{S}_c$ are the S isotopic conditions of the uncontaminated magma (0 ‰) and the local sediment, respectively (-20.4 to -9.9 ‰). X_m and X_c are the concentrations of S in the magma and sediment, respectively. Figure 12 shows a binary mixing model between the sill and sedimentary sulfur, based on the calculation above. The upper margin of the sill contains around 8 ‰ sedimentary sulfur, whereas the lower margin contains only 1 ‰ . Around 0.8 ‰ of the sulfur in the olivine gabbro samples comes from sedimentary sulfur, and the gabbro samples contain almost no sedimentary sulfur (0.05 ‰). It follows that the margins of the intrusion will have had a greater degree of crustal interaction and S assimilation. The

diffusion of volatiles at the margins of the hot intrusion could have promoted the transfer of S both from and into the proximal sediment (Penniston-Dorland et al. 2008), while direct assimilation of crust would provide larger abundances of S more rapidly (Robertson et al. 2015). Marginal dolerite $\delta^{34}\text{S}$ deviates strongly from ‘mantle-like’ values (Sakai et al. 1984). Despite being the only positive magmatic sample, gabbro sample T2 appears too isotopically heavy to have a purely magmatic signature. However, a small amount of evaporitic material (known to be in the country rocks; Wilson, 1979) may be responsible for the anomalously positive $\delta^{34}\text{S}$ value (e.g. Ripley et al. 2003).

The dominance of S isotope values less than -2.5 ‰ in sulfides in the intrusion (Supplementary Table S3) indicate that widespread contamination by up to 8 % crustal sulfur (Fig. 12) occurred in the ascending magma at varying depths in the underlying magma plumbing system. Despite this reasonably consistent contamination signature, highly variable sulfide S/Se ratios between olivine gabbros and the rest of the sill suggest that the history of magma contamination in the Magilligan Sill is more complicated than S isotopes imply (Fig. 9b). With the exception of the olivine gabbros, all sill units have S/Se between 3 510 and 25 200, strongly skewed to higher values that are far removed from the mantle norm of 2 850-4 350 (Eckstrand and Hulbert 1987, Queffurus and Barnes 2015). Only the olivine gabbros (S/Se ranging from 1 980 to 3 720) appear to have retained a ‘mantle-like’ sulfide S/Se signature, despite crustal isotopic input. Modelling the Pd, Se and S/Se concentrations of olivine gabbro and gabbro sulfides yields that they are likely to have had R-factors of around 500-1 000 and 10-100, respectively. Modelling results are shown in Supplementary Material S5 and use methods described by Lesher and Burnham (1999).

If the sill lithologies represent separate magma pulses (e.g. Fig. 11), the S/Se discrepancy may be the result of largely different degrees of contamination (which contradicts $\delta^{34}\text{S}$ signatures in Fig. 9) or, more likely, different S-saturation processes in each pulse

(indicated by different R-factors). Olivine gabbro sulfides have evidently lost S (e.g. low S/Se) which could be due to ‘cumulative R-factor’, a process described by Kerr and Leitch (2005). Sulfide liquids formed during contamination-driven S-saturation in the ascending magma may be cycled upwards in the plumbing system by subsequent magma pulses, towards their final resting horizon (e.g. Hayes et al. 2015). This will subject them to multistage dissolution upgrading, wherein the sulfides are partially dissolved during transportation, reducing their volume and S content while retaining their chalcophile element concentrations (e.g. PGE and Se) (e.g. Kerr and Leitch 2005, Naldrett 2010). We propose that olivine gabbro sulfides in the Magilligan Sill formed in this manner.

It should be noted that S loss and low S/Se in sulfides could also be induced by post-magmatic partial oxidation of sulfide minerals, unrelated to S-saturation events (Peck and Keays 1990, Dunn 1997, Queffurus and Barnes 2015). While minor oxidation of sulfides is observed in the olivine gabbros (10-20 %), oxidation is unlikely to explain the significantly lower S/Se ratio of these sulfides in comparison to those in the rest of the sill. For example, if a sulfide grain from a gabbro (initial S/Se = 10 600) undergoes 20% S loss, this would decrease the S/Se to 7 610. In the olivine gabbros, the mean S/Se ratio is 2 940 and if this were to be produced by oxidation of gabbro sulfides alone, it would require a S loss of 72%. Such oxidation should leave clear and visible signs in the olivine gabbro sulfides (e.g. oxide minerals), for which there is no evidence. We conclude that cumulative R-factor is the most likely cause of ‘mantle-like’ S/Se ratios in the Magilligan Sill.

In contrast to sulfides in the olivine gabbros, the lack of detectable trace metals and high S/Se in sulfides from the dolerites and gabbros of the sill (Fig. 10) may imply that this generation of magma remained S-undersaturated throughout ascent, only forming sulfides very locally when contaminated by crustal S from the Waterloo Mudstones at the level of final emplacement. This would inhibit chalcophile sequestration and cumulative R-factor upgrading

via magma transportation (as envisaged for the olivine gabbro sulfides) (Robertson et al. 2015). This shallow, local S-saturation model is similar to that predicted for basalt dykes on the Isle of Skye (Hughes et al. 2015a). In this way, sulfide (pyrite) formation is akin to very late-stage magmatic-hydrothermal sulfide formation – there was no circulation of sulfide liquid in the magmatic intrusion or feeder and hence no opportunity to equilibrate with the host silicate magma and its chalcophile element content, resulting in base/precious metal poor pyrite. If the base/precious metal bearing second generation sulfides were cycled from upstream in the plumbing system, they may be found in higher (potentially economic) abundances below or adjacent to the Magilligan Sill horizon (e.g. ‘earlier’ in the system). The change in $\delta^{34}\text{S}$ in Figure 10 could potentially represent a diffusion profile, in which the outer parts of the sill (e.g. the dolerites) volatilise and assimilate the most crustal S, reflected in high S/Se and negative $\delta^{34}\text{S}$ values that gradually shift to more S-poor values towards interior gabbros. Olivine gabbros disrupt the profile trend, further supporting the hypothesis that they are of a separate injection of magma and different saturation events. Although diffusion via contact metamorphism is a slow process compared to direct crustal assimilation (Robertson et al. 2015), field evidence of the Trotternish Sills report 50-200 cm baked margins of hardened country sediment with minimal surviving sulfide minerals adjacent to the intrusions (e.g. Gibson and Jones 1991, Hughes et al. 2015a). This feature strongly indicates S diffusion was important in triggering S-saturation in Trotternish magmas. Given that there are hornfelsed margins immediately next to the Magilligan Sill, we suggest similar processes could have contributed here too within a comparable timescale.

Magmatic model

By combining the silicate and sulfide petrography and sulfide compositions, we envisage a final two-stage development model for the Magilligan Sill (Fig. 13). In Stage A, S-undersaturated magma from a deep magma reservoir was emplaced as a sill into the Waterloo

490 Mudstones. Significant contamination of the magma by crustal S only occurred at the current
 491 level of emplacement, through contact with the Waterloo Mudstones. This contamination
 492 occurred via volatilisation of S from the country rock due to contact metamorphism, or via S
 493 addition by direct crustal assimilation. This process was so late-stage and localised that the
 494 sulfides within the sill formed under magmatic-hydrothermal conditions. This means that no
 495 significant transportation of the sulfide liquid took place within the magma, and little
 496 chalcophile elements (for which we use Se as a proxy) entered the sulfide (leading to high S/Se
 497 ratios from 3 510 to 25 200 and $\delta^{34}\text{S}$ of -9.6 to -2.5 ‰ in the dolerites and gabbros). As a result,
 498 sulfides (pyrite and pyrrhotite) crystallising from the S-saturated magma did not sequester
 499 chalcophile elements successfully (Naldrett 2010).

500 In the time between the Stage A and B, the dolerites and gabbros were hydrothermally
 501 altered (perhaps synchronously with local S volatilisation and pyrite formation) to produce
 502 abundant chlorite and clays, and altering olivine phenocrysts to serpentine. In Stage B (Fig.
 503 13), the source composition of the magma supply in the conduit system shifted to a more
 504 primitive composition so that subsequent magma replenishment in the Magilligan Sill formed
 505 the olivine gabbros. S-saturation likely occurred earlier (perhaps deeper) in the magma
 506 plumbing system, as indicated by the upgrading processes envisaged for sulfides in the olivine
 507 gabbros. Evaporites and mudstones in the Triassic Mercia Mudstone Group or the Permian
 508 Belfast Group hundreds of metres below the Magilligan Sill could perhaps have supplied
 509 crustal S to Stage B magma, driving it to S-saturation deeper in the system (GSNI 2004).
 510 Sulfides (including pyrite, pyrrhotite, chalcopyrite and pentlandite) that segregated from the
 511 silicate melt in Stage B contain higher abundances of Ag (< 88 ppm), Co (< 1 460 ppm), and
 512 PGE (< 4 ppm). We propose that these sulfides were originally mineralised ‘upstream’ in the
 513 plumbing system that fed the Magilligan Sill. They were cycled through subsequent pulses of
 514 second-generation magma before being entrained and emplaced into the Magilligan Sill. The

pre-existing dolerites and gabbros formed during Stage A most likely shielded this second pulse of magma (Stage B) from further S absorption from the local country rocks, preventing dilution or addition of late-stage magmatic-hydrothermal S.

In this way, the Magilligan Sill, unlike the Trotternish Sills, retains evidence for multiple S-saturation events and pathways between various episodes of magmatic replenishment, as represented by discrete silicate magma pulses. The Southern Feeder Dike Complex of Victoria Island in Canada (part of the Franklin Large Igneous Province) has been interpreted in a similar way, also featuring evidence of conduit-focused magma replenishment and sulfide cycling at different depths in its plumbing system (Hayes et al. 2015). Given that the second-generation sulfides contain PGE, Ni, Cu, Co, and Ag, a higher volume concentration of *in situ* mineralisation of similar or higher tenor nearer the depth at which S-saturation occurred could provide an interesting target for further exploration, despite the Magilligan Sill itself being sub-economic. Since the relatively thin (compared to the southwest) Carboniferous limestones in County Londonderry overlie Proterozoic Grampian basement and both of these contain few S-rich lithologies (GSNI 2004), Permian and Triassic sediments above these appear to be the most logical exploration target for Stage B sulfide-bearing intrusions. Halite beds in the White Brae Mudstone Formation (Permian), sabkha mudstones and halite beds in the Craiganee Formation (Middle Triassic) or dark mudstones in the Westbury Formation (Upper Triassic) are all suitable crustal S contaminants (Wilson 1972). A deeper level of the Magilligan plumbing system in contact with one of these units could potentially be the S-saturation horizon for the olivine gabbro sulfides, and should be the key exploration target for any further Ni-Cu-PGE investigations in the area.

Conclusions

538 The identification of discrete magmatic pulses within the Magilligan Sill indicate that
 539 at least two chemically distinct magma generations were emplaced within a single intrusion.
 540 These magma batches may have had significantly different S-saturation pathways and
 541 correspondingly different mineralisation potentials. The first magmatic generation crystallised
 542 to form most of the sill – olivine-deficient, highly altered dolerites and gabbros with barren
 543 sulfide minerals. The second generation crystallised to form olivine gabbro horizons within
 544 the pre-existing sill, and contained metal-enriched sulfides. In order to form younger, more
 545 primitive magmas, the feeder chamber must have mixed with a new magma between the
 546 emplacements of the two different units in the sill, in a similar fashion to the Antrim Plateau
 547 Lavas, in which mafic Upper Basalts postdate less mafic Lower Basalts.

548 The S-isotope composition ($\delta^{34}\text{S}$) of the Magilligan Sill indicates that crustal S
 549 contamination is present throughout the entire intrusion. S/Se ratios in second-generation
 550 (olivine gabbro) sulfides are similar to that of published average ‘magmatic’ values of 2 850-4
 551 350 (Eckstrand and Hulbert 1987, Queffurus and Barnes 2015), indicating a deeper S-
 552 saturation event perhaps with smaller degrees of crustal contamination. For this reason, sulfides
 553 found in the olivine gabbro sections of the sill are interpreted to have formed at depth before
 554 being cycled upstream by later magma pulses. The possible controls on this deep S-saturation
 555 include: the changing initial composition of the magma at source; the amount of sedimentary
 556 S available to the magma via assimilation, and the degree of shielding from these sediments
 557 enforced by pre-existing layers of the sill; and the geometry of the magmatic plumbing system.
 558 Through a combined approach of S-isotopes, S/Se ratios and detailed petrography, the
 559 pathways to S-saturation may be determined within plumbing systems and valuable
 560 information fed back into the exploration industry with regards to vectoring towards
 561 orthomagmatic sulfide mineralisation, both in the BPIP and more generally for large igneous
 562 provinces.

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Table 1 – Average LA-ICP-MS trace element concentrations of sulphides within upper and lower dolerites, gabbros, olivine gabbros and country sediment. * - calculated stoichiometrically. † - average concentration of detected isotopes. S = 53.45 wt. % \approx pyrite; S = 34.94 wt. % \approx chalcopyrite.

Lithology	S* Wt. %	S/Se	Fe Wt. %	Ni Wt. %	Cu Wt. %	Co ppm	Zn ppm	As ppm	Se ppm	Ru† ppm	Rh† ppm	Pd† ppm
U. Dolerite	53.45	14 279.29	48.60	0.19	0.04	535.455	510.54	19.40	43.32	-	-	-
Gabbro	53.45	10 635.11	44.37	-	0.05	100.70	241.80	20.67	56.21	-	-	-
O. Gabbro	34.94	2 943.03	48.72	6.86	9.26	1 454.59	3 922.32	-	122.89	0.1	0.33	0.64
L. Dolerite	53.45	11 595.33	52.54	0.33	0.10	727.30	3 492.78	355.99	44.79	-	-	-
Sediment	53.45	8117.503	45.02	0.10	0.07	594.90	117.55	1962.31	74.23	-	-	-

Sample	Ag ppm	Cd ppm	Sb ppm	Te ppm	Re ppm	Os ppm	Ir ppm	Pt ppm	Au ppm	Bi ppm	ΣPGE ppm
U. Dolerite	0.94	-	1.74	-	0.2	-	-	-	0.01	0.05	-
Gabbro	2.93	-	3.48	0.86	0.12	-	-	-	-	0.15	-
O. Gabbro	68.54	29.65	0.35	6.00	0.32	0.04	0.04	0.36	0.05	0.88	1.51
L. Dolerite	0.50	-	8.2	0.45	0.02	-	-	-	0.04	0.04	-
Sediment	6.38	0.86	85.59	6.38	0.06	-	-	0.05	0.91	0.65	0.05

Table 2 – Summary S-isotopic compositions of sill and country rock lithologies.

Lithology	Min $\delta^{34}\text{S}$ ‰	Max $\delta^{34}\text{S}$ ‰	Mean $\delta^{34}\text{S}$ ‰	n
Shale (above sill)	-10.00	+5.30	-5.95	4
Upper dolerite	-9.60	-2.50	-6.58	5
Gabbro	+3.40	+3.40	+3.40	2
Olivine Gabbro	-2.50	-1.10	-1.80	2
Lower Dolerite	-2.50	-2.50	-2.50	1
Shale (below sill)	-20.40	-14.90	-17.63	8
<i>Magilligan Sill</i>	-9.60	+3.40	+3.10	22
<i>(overall)</i>				

Figure Captions

Figure 1 – Schematic map of the geology of the BPIP, showing basement units, onshore lavas and notable intrusive complexes. Inset map gives the subdivisions of the Antrim Plateau lavas and the location of the Magilligan and Portrush Sills. Based on work by Woodcock and Strachan (2012).

Figure 2 – Schematic geological map of the Magilligan Peninsula, Northern Ireland, indicating the location of the Magilligan Sill and Boreholes 1-3.

Figure 3 – Simplified lithological logs of the Magilligan, Portrush and Trotternish Sills, with their relative intrusion level within the Jurassic stratigraphic columns for Scotland and Ireland. Sill packages are stylised to show multiple injection events. Formation names from Woodcock and Strachan (2012) and GSNI (2004). Portrush and Trotternish relationships from Ledevin (2012), and Gibson and Jones (1991), respectively.

Figure 4 – Representative composite geological log of the Magilligan Sill boreholes. "T" labels show the analysed thin section sample numbers and locations.

Figure 5 – Photomicrographs of Magilligan Sill thin sections: a) Olivine-deficient gabbro (T3) [transmitted light XPL]; b) Olivine gabbro (T7) [transmitted light XPL]; c) Small pyrite grains within gabbro (T2) [reflected light]; d) Large sulphide amalgamation within olivine gabbro, [back-scattered electron image, BSE] (T2). [Pl – plagioclase, Cpx – clinopyroxene, Ol – olivine, Py – pyrite, Po – pyrrhotite, Ccp – chalcopyrite, Pn – pentlandite, Gn – galena]

Figure 6 - Bivariate geochemical plots of a) MgO vs. CaO and b) MgO vs. FeO in analysed clinopyroxenes.

Figure 7 – Bivariate geochemical plots of sulphides in the Magilligan Sill: a) Ni vs. Co; b) Ni vs. Ag; c) Cu vs. total PGE; d) Fe vs. total PGE with respect to mineral phases. Gabbro samples do not contain detectable Ni or PGE.

Figure 8 – Bivariate geochemical plots of sulphides in the Magilligan Sill: a) Se vs. Ni/(Fe+Ni+Cu); b) Se vs. total PGE; c) S/Se vs. total PGE with respect to mineral phases.

Figure 9 – a) Histogram of $\delta^{34}\text{S}$ compositions of sulphides in the Magilligan Sill. b) Combined $\delta^{34}\text{S}$ vs. S/Se plot for sulphides in the Magilligan Sill, with published magmatic values from Seal (2006) and Quefferus and Barnes (2015). Crosshatched area represents typical magmatic/mantle values.

Figure 10 – Representative downhole variations in lithology (not to scale) combined with S/Se, $\delta^{34}\text{S}$, total PGE, Ni, Ag and Cu data from sulphides in these lithologies. Arrows on S/Se and $\delta^{34}\text{S}$ plots describe the suggested diffusion profile grading inwards from dolerite to gabbro.

Figure 11 – Petrological development of the Magilligan Sill, showing the two lithological phases found in the intrusion. [Pl – plagioclase, Cpx – clinopyroxene, Ol – olivine, Srp – serpentine, Chl – chlorite, Spl – spinel, Py – pyrite, Po – pyrrhotite, Ccp – chalcopyrite, Pn – pentlandite]

Figure 12 – Binary mixing model for the Magilligan Sill and sedimentary sulphur.

Figure 13 – Stage A in the magmatic development model for the Magilligan system, showing the formation of the dolerites and gabbros, and their barren sulphides. Stage B in the magmatic development model for the Magilligan system, showing the formation of the olivine gabbros, and their cycled base/precious metal sulphides. Model constructed with reference to similar systems in Barnes *et al.* (2016).

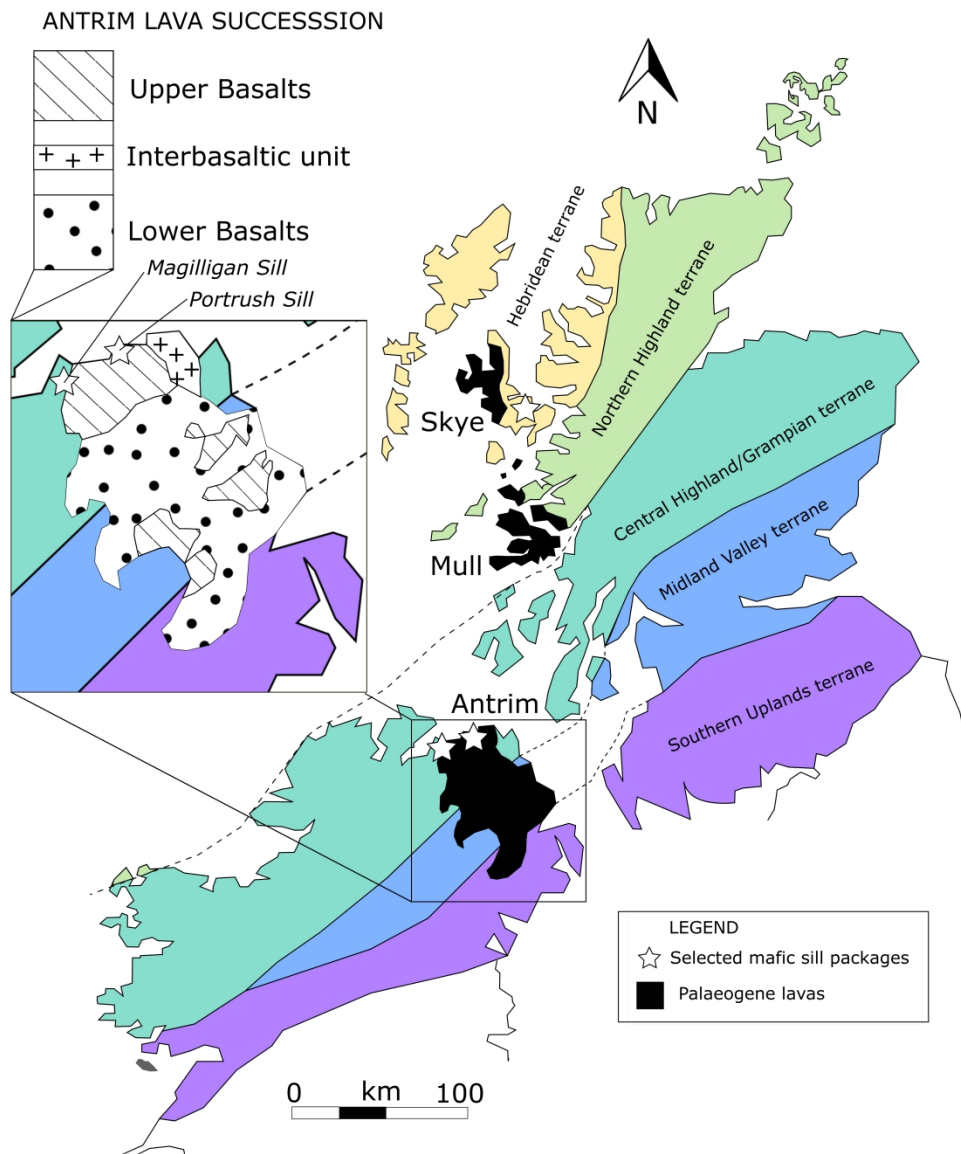


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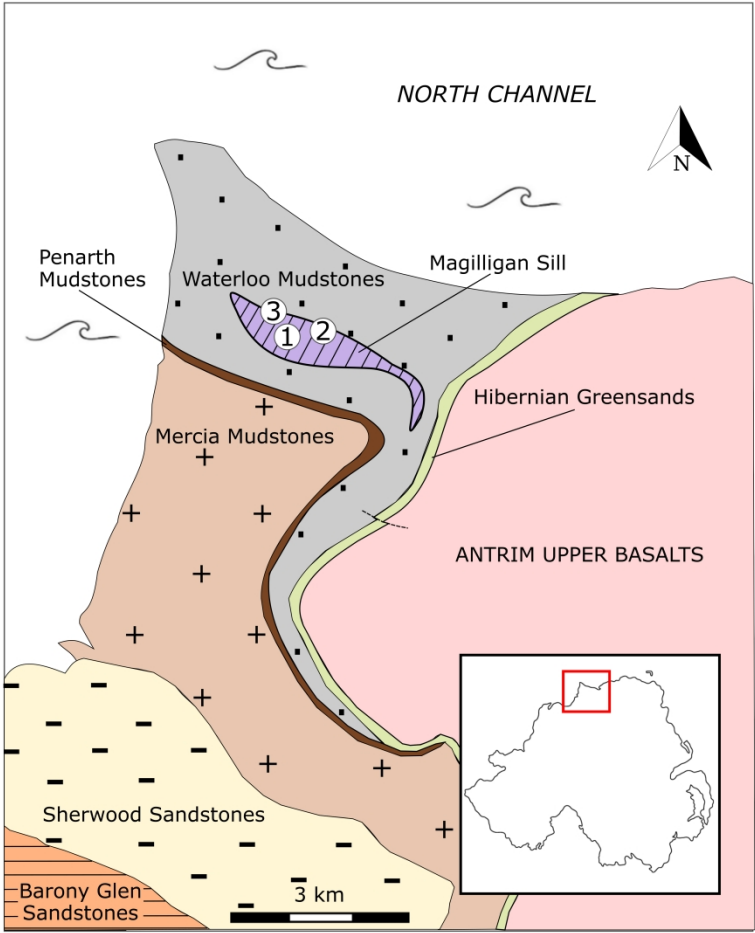


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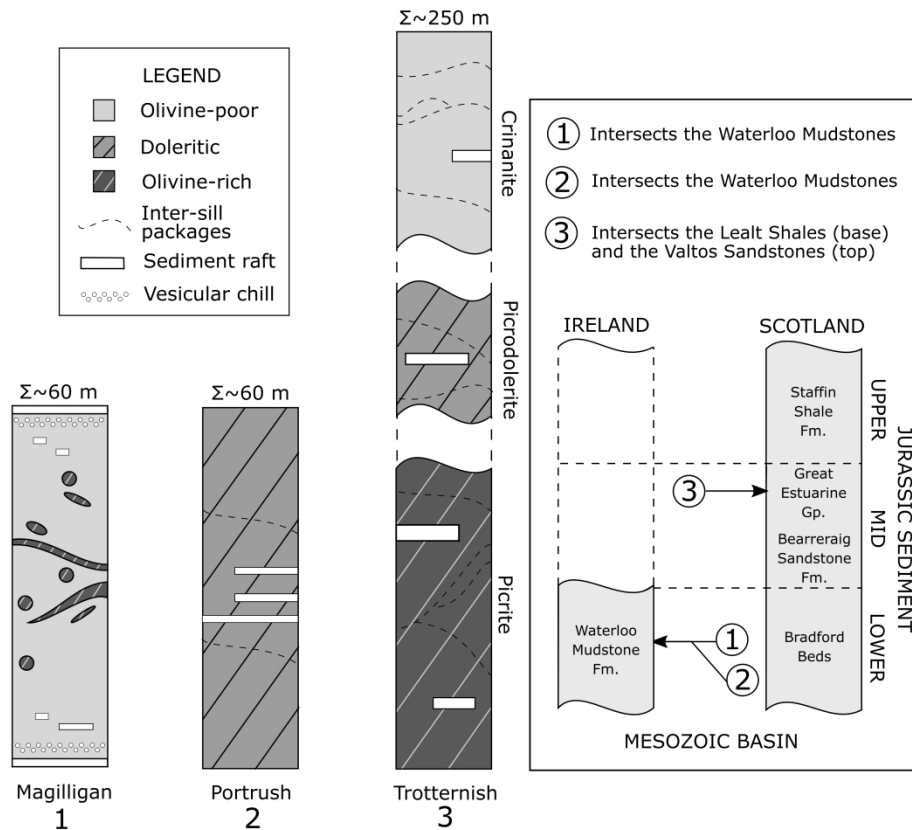


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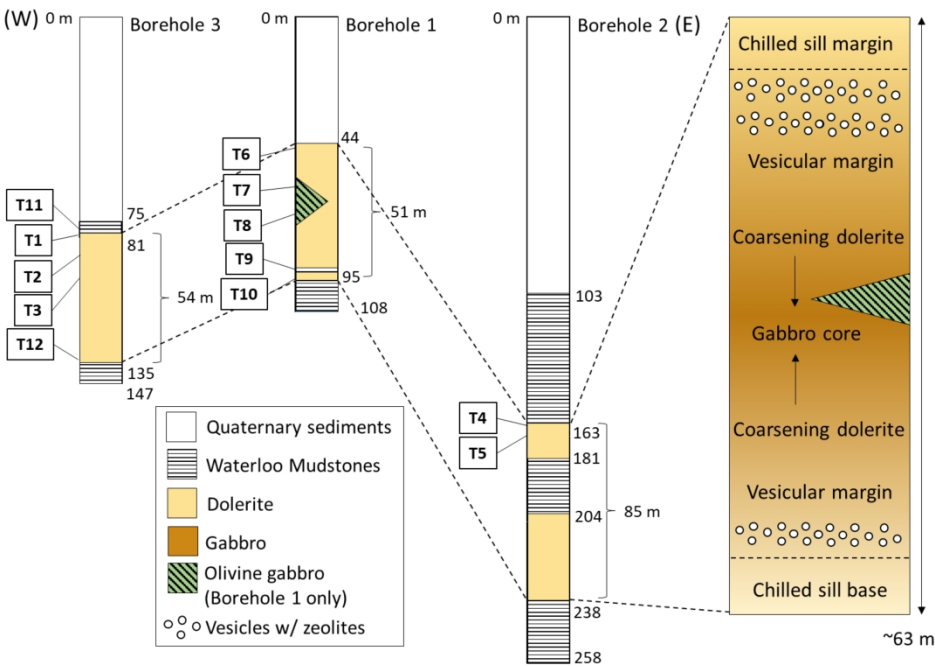


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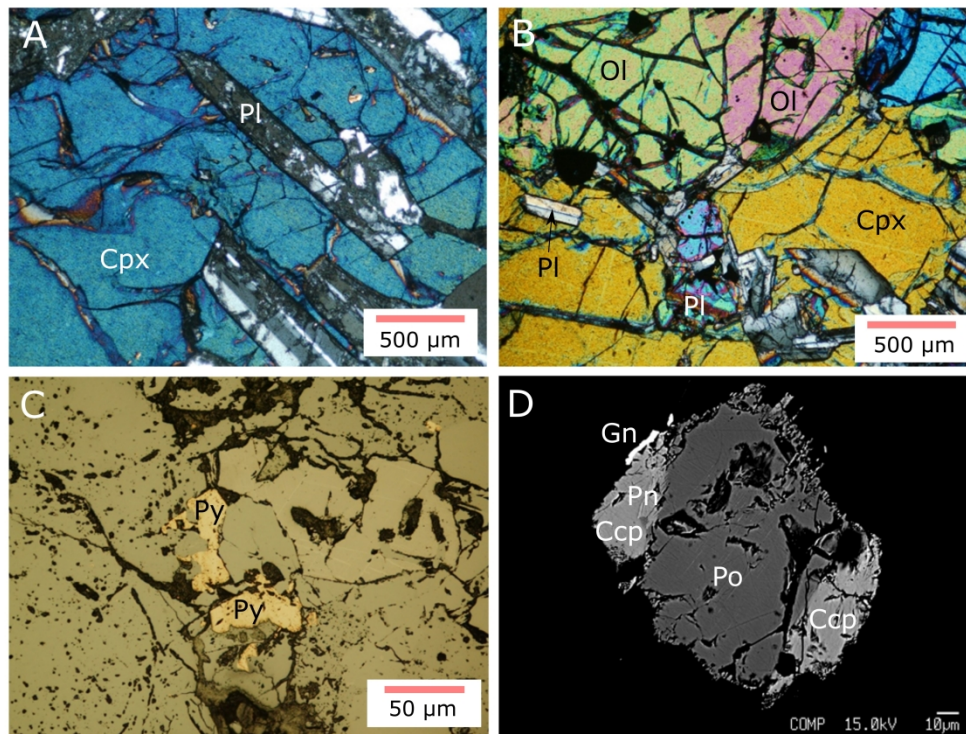


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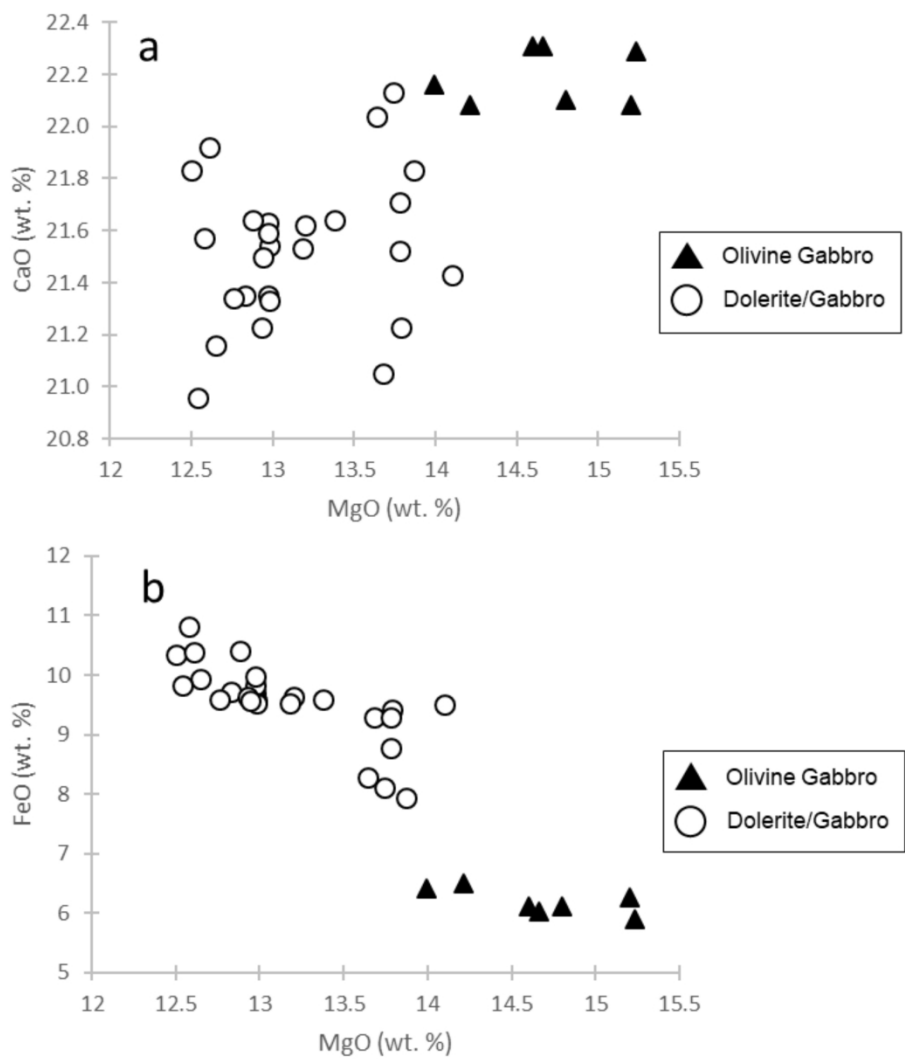


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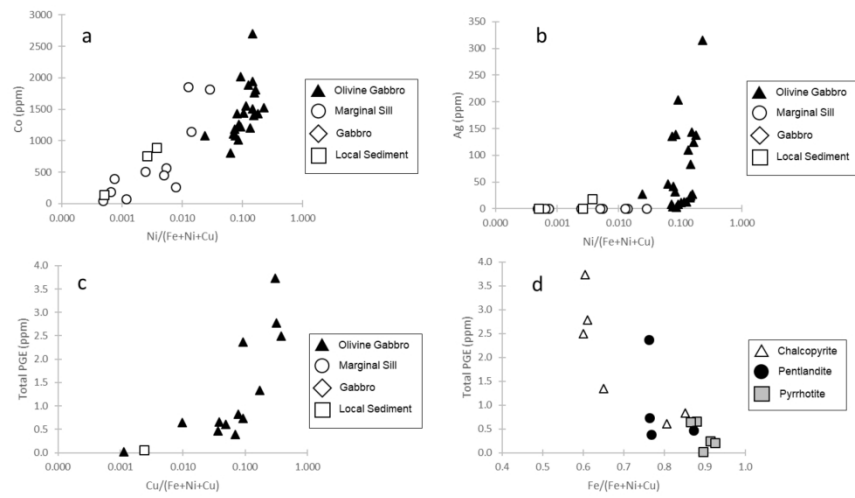


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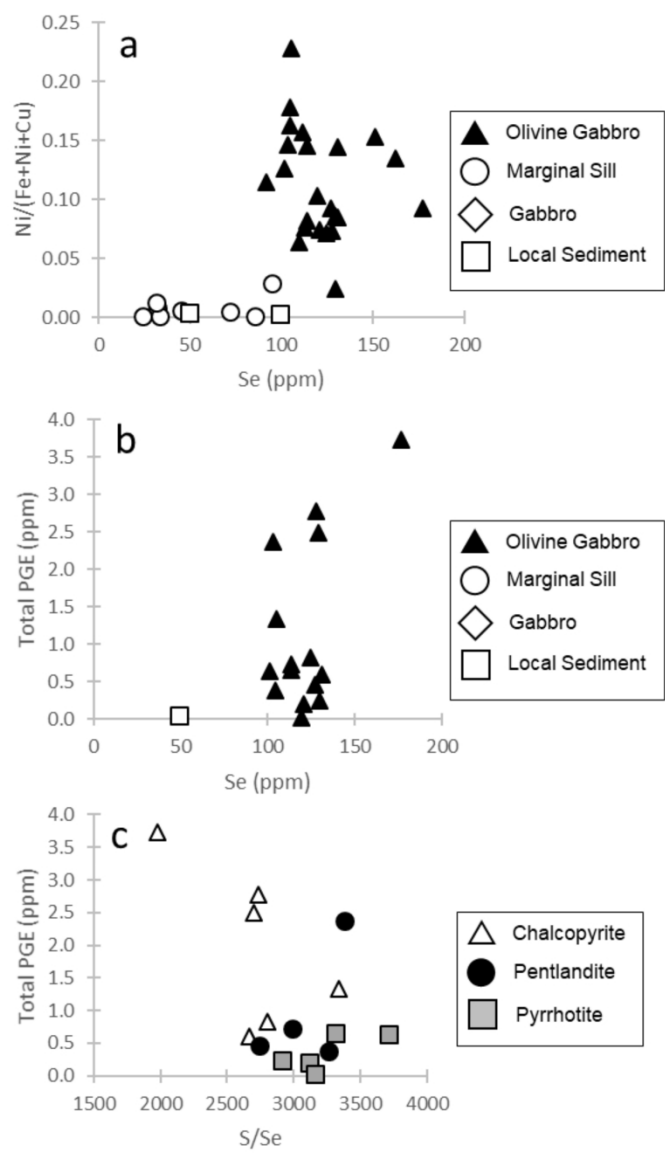


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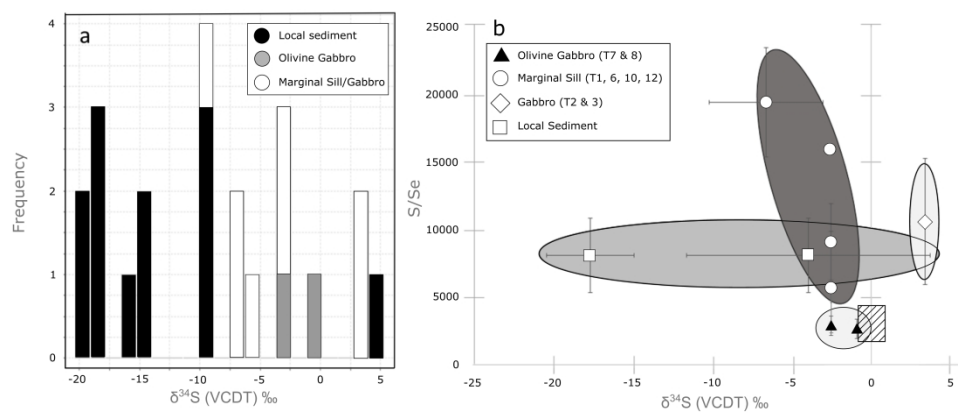


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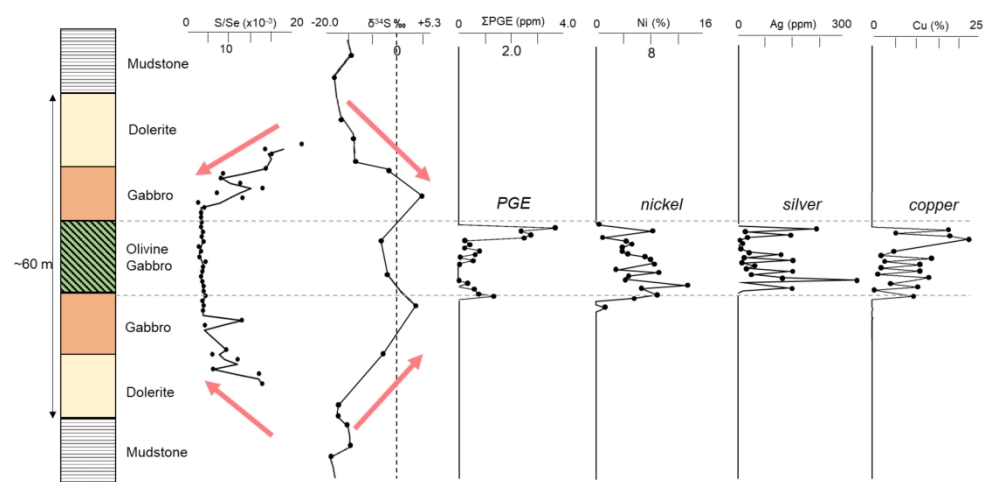


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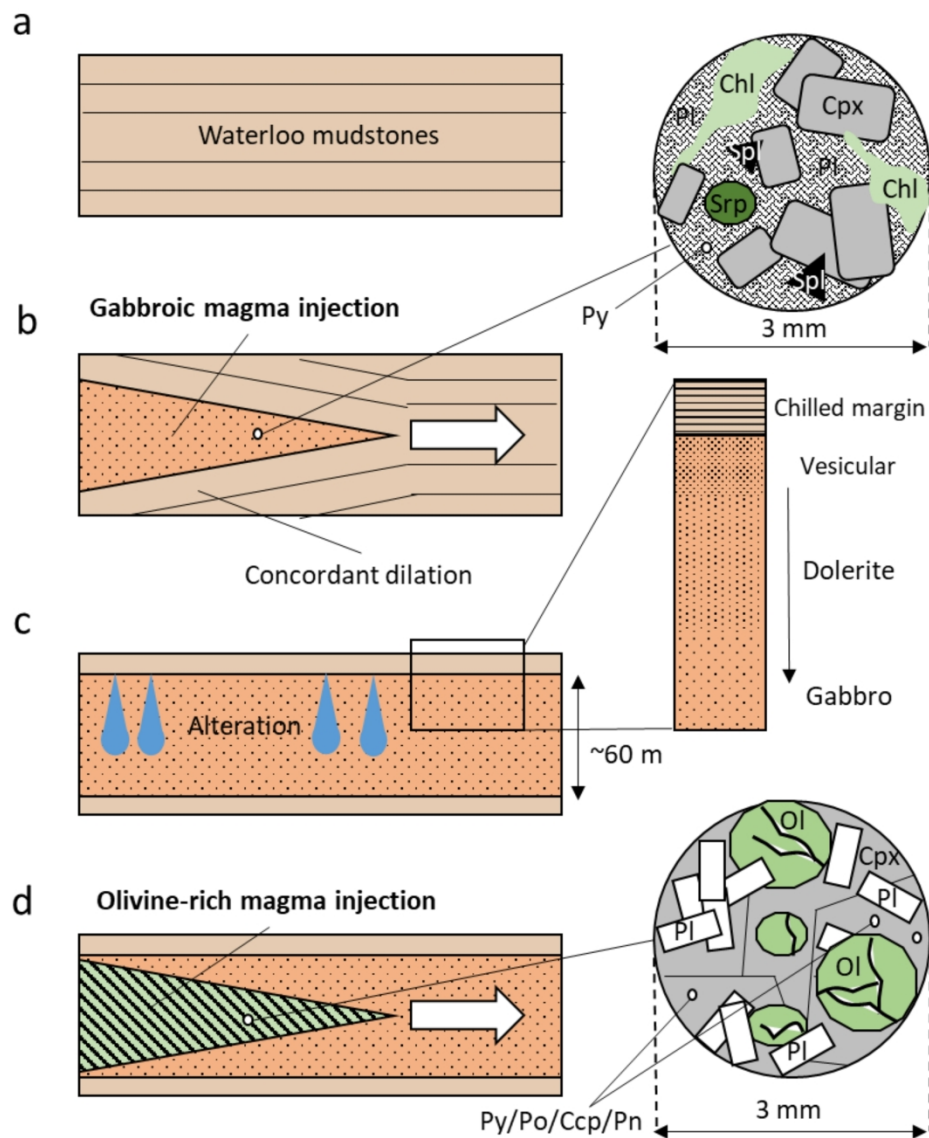


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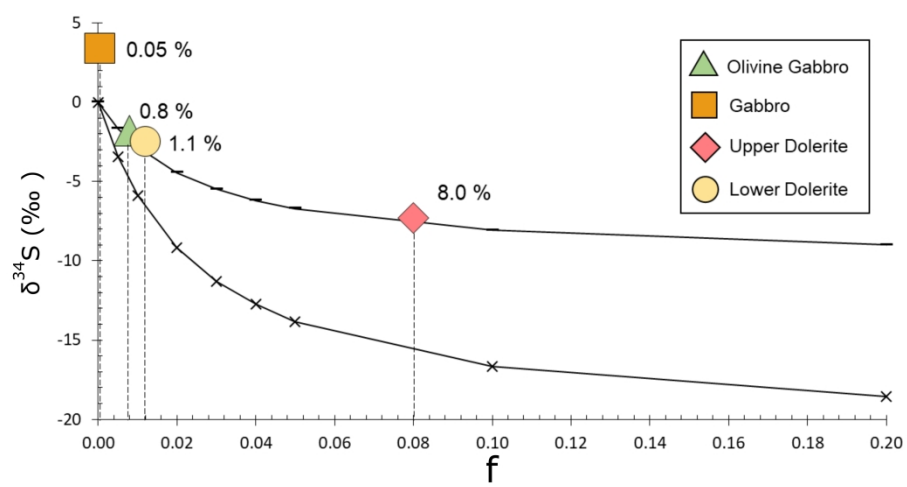


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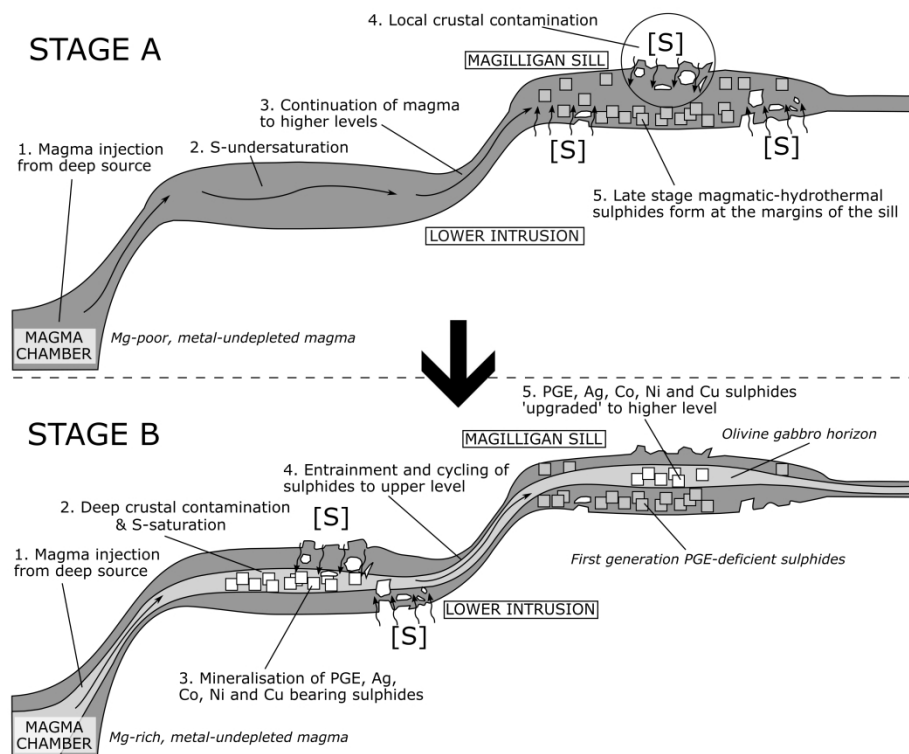


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